Flame Emission Studies of Ozone with Metal Alkyls: $Zn(CH_3)_2$ and $Zn(C_2H_5)_2$

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Resolved flame emission spectra from the reaction of ozone, O_3, with zinc dimethyl, $Zn(CH_3)_2$, and zinc diethyl, $Zn(C_2H_5)_2$, in a flow system at about one torr pressure reveal a number of interesting electronically-excited species. The $Zn(CH_3)_2 + O_3$ flame has a pale blue appearance, characteristic of the "cool flame" bands of CH_2O, while the $Zn(C_2H_5)_2 + O_3$ flame has a deep blue appearance caused by ZnH* emission. In addition the reaction of O_3 with H atoms resulting probably from the decomposition of C_2H_5 radicals in the latter reaction leads to strong $OH^\dagger$ ($^2\Pi_i$) emission (Meinel bands). Also, OH* ($^2\Sigma^+$) emission is observed and is found to have a quadratic dependence on $OH^\dagger$. Mechanisms involving the different chemistry of CH_3 and C_2H_5 radicals in the flame are proposed to account for these observations.

I. Introduction

The gas-phase reactions of ozone with saturated and unsaturated hydrocarbons [1] have received rather careful attention from several workers interested in the general nature of combustion. Premixed [2, 3] and diffusion [4] flames of metal alkyl compounds have been carried out to determine such properties as ignition temperatures and burning velocities.

More recently, as part of a general intensive effort to develop electronic-transition chemical lasers, several groups [5-7] are again focusing their attention on the reactions of spontaneously flammable metal alkyl compounds with powerful oxidizers, notably ozone and fluorine. However, practically no attempt has been made to determine the mechanism of these reactions from the existing spectroscopic data. Although none of the emitting species produced in the gas-phase reactions studied so far have been shown to exhibit population inversions, we deem it necessary to investigate these reactions for we believe that the information thus gathered can shed new light not only on the nature of metal-alkyl reactions in particular, but also on the chemistry of combustion in general.

Flame studies are generally complicated by the background radiation associated with elevated temperatures and by the profuse number of chemical species present. Thus it would be advantageous to study the combustion of polyatomic molecules under single-collision conditions, i.e., at pressures below 1 mtorr. However, no visible emission from such reactions can be observed for the simple reason that most electronically-excited species can only result from secondary or even tertiary reactions.

There are also good reasons why one should turn to O_2 as the oxidizing agent in these studies, but several workers [5, 6] have also found, in agreement with our own observations, that no chemiluminescence results from the reactions of O_2 with spontaneously flammable fuels at pressures ca. 1 torr. Nor could emission be seen using N_2O as the oxidizer. Thus we chose to use O_3 and to work at the minimum pressure at which emission sets in – about 0.5 torr in both reactions considered here.

II. Experimental

Figure 1 shows a schematic diagram of the experimental set-up. A glass sphere (125 cm^3) forms the

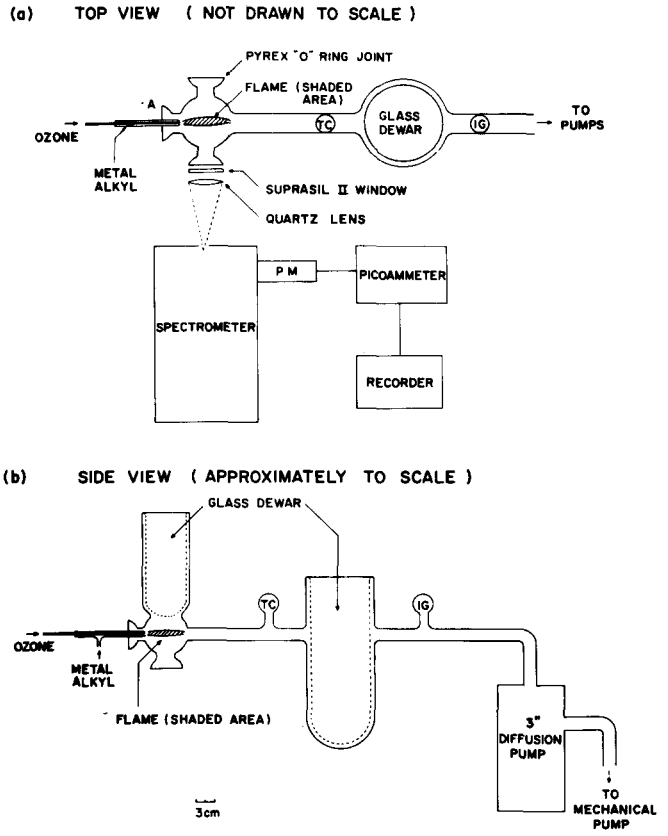

Fig. 1. Experimental arrangement: (a) top view; and (b) side view. Here TC = thermocouple gauge, IG = ionization gauge, and PM = photomultiplier tube.

reaction chamber. Four Pyrex "O" ring joints are joined onto this sphere to house the viewing windows and the flange for the reagent flow inlets. A glass dewar of 350 cm^3 capacity is positioned vertically on the glass sphere. An uncalibrated thermocouple gauge (Veeco TG-7) monitors the pressure 16 cm downstream from the reaction zone. Further downstream, a larger glass dewar of 750 cm^3 capacity traps most of the organic reaction products. These dewars are cooled to -78°C.

Diethyl zinc, obtained from Texas Alkyls, Inc., and dimethyl zinc, obtained from Alfa Products, Inc., are used as received. Both vendors list the purity of these compounds as greater than 98%.

Ozone is generated with a Welsbach (Model T-408) ozonator and collected on silica gel cooled to -78°C by a slurry of dry ice and acetone. Immediately prior to the run, the ozone trap is briefly opened to the pumps to remove excess O_2.

The reaction chamber is initially pumped down to less than 1 mtorr by a 1405B Welch pump aided by a 3 in diffusion pump. The reactants are introduced through two concentric glass nozzles of diameters 1.0 and 3.0 mm. The nozzles are held by Cajon ultra-torr adapters onto the "O" ring joint marked *A* in Fig. 1 which facilitates removal for cleaning and depth adjustment during a run. The metal alkyl compound, kept in a 20 cm^3 glass cell, is introduced into the reaction region through the outer nozzle at a pressure between 10 and 50 mtorr. Usually ozone is flowed in through the inner nozzle, but the emission is independent of the nozzle in which a reactant is introduced. To ensure fairly complete combustion of the metal

alkyls, the pressure of ozone is maintained at about 0.8 to 1.0 torr, essentially equivalent to the total pressure in the reaction chamber.

The flame emission is spectrally resolved from 2800-8400 Å using a 1 m Interactive Technology Czerny-Turner spectrometer operated in first order with a Bausch and Lomb 1200 groove/mm grating blazed at 5000 Å. A Centronic S-20 photomultiplier (with extended red response) inside a cooled housing ($\approx -30°C$) is attached to the exit slit of the spectrometer. The signal from the photomultiplier is detected by a Keithley 417 fast picoammeter whose output signal drives a Hewlett-Packard 7100B strip chart recorder. The latter provides a tracing of the spectrum.

When the metal alkyl is present in the reaction zone, emission is produced spontaneously as soon as ozone is introduced. During the entire scan of the emission, the flame has the appearance of a narrow horizontal luminous strip (jet) approximately 5 mm wide and 3 cm long. To avoid the complication of wall reactions we have made certain that the flame does not touch the reactor walls.

III. Results and Discussion

The flame from the reaction $O_3 + Zn(CH_3)_2$ has a pale blue color at a total pressure of about 1 torr. The diffusion flame from the reaction $O_3 + Zn(C_2H_5)_2$ is marked by a deep blue color as a result of intense emission of ZnH in the 4100-4300 Å region.

A. $O_3 + Zn(C_2H_5)_2$ Reaction

Figure 2(a) shows the spectrum of the $O_3 + Zn(C_2H_5)_2$ chemiluminescence at about 1 torr pressure; the emitting species $Zn(^3P_1)$, $OH^\dagger$ ($^2\Pi_i$), and $ZnH(^2\Pi)$ are readily identified.

Early studies on the reactions of $Zn(CH_3)_2$ with O_2 at torr pressures [8-10] show that the reaction product has the approximate composition $Zn(CH_3)_2 \cdot 2O_2$. We can only speculate on the primary steps of these reactions, the initial step most probably involving the attack of the oxidizer O_2 or O_3 on the central zinc atom. If such is the case, the result could be the insertion of an O atom between a Zn-C bond or the rupture of the latter to form ZnC_2H_5.

1. Acetaldehyde Emission (?)

The broad emission band from 4350-4700 Å shows some diffuse vibrational structure (Fig. 3) and the emitter is believed to be due to acetaldehyde. The energy required to excite this species to the $\tilde{A}$ state, about 82 kcal/mole, can amply be supplied through the exothermic reactions

$$CH_3CH_2O\cdot + \cdot OH \rightarrow CH_3CHO^* + H_2O, \quad (1)$$

and

$$CH_3CH_2O\cdot + CH_3CH_2O\cdot \rightarrow CH_3CH_2OH + CH_3CHO^*. \quad (2)$$

We have no direct evidence of the species $CH_3CH_2O\cdot$ being present in the flame. However, there is evidence that the cool flame bands of CH_2O in other flames come from an analogous mechanism [11].

2. OH ($^2\Pi_i$) Meinel Bands

The well-resolved bands from 5600 to 8400 Å, shown in Fig. 4, are definitely caused by emission from OH ($^2\Pi_i$). The large doublet splittings are easily resolved using 500μm spectrometer slits, corresponding to a spectral resolution of about 5 Å. From analysis of the intensities of these bands, we see that $v = 9,8$, and 7 are preferentially populated. This suggests that $OH^\dagger$ is produced in the following reaction [12-13]:

$$H + O_3 \rightarrow O_2 + OH^\dagger \ (v=8,9); \ \Delta H = -77 \text{kcal/mole}. \quad (3)$$

The likely source of H atoms is the decomposition of C_2H_5 radicals to yield ethylene (C_2H_4) and H.

3. OH ($^2\Sigma^+$) and Zn ($^3P_1$)

Although the OH bands from 3000 to 3080 Å are completely obscured by the intense Zn line (Fig. 5), we can nonetheless obtain a fairly good estimate of the OH rotational temperature by examining the well-resolved *P* branch of the (0,0) band lying between 3100 and 3300 Å. Our analysis shows T_{rot} to be 2000-2200°K (Fig. 6). This value is well below that reported by Benson, et al. [6] from studies of F_2/O_2 + metal alkyl flames, where they measure T_{rot} of OH to be $\approx$4000°K. It is well

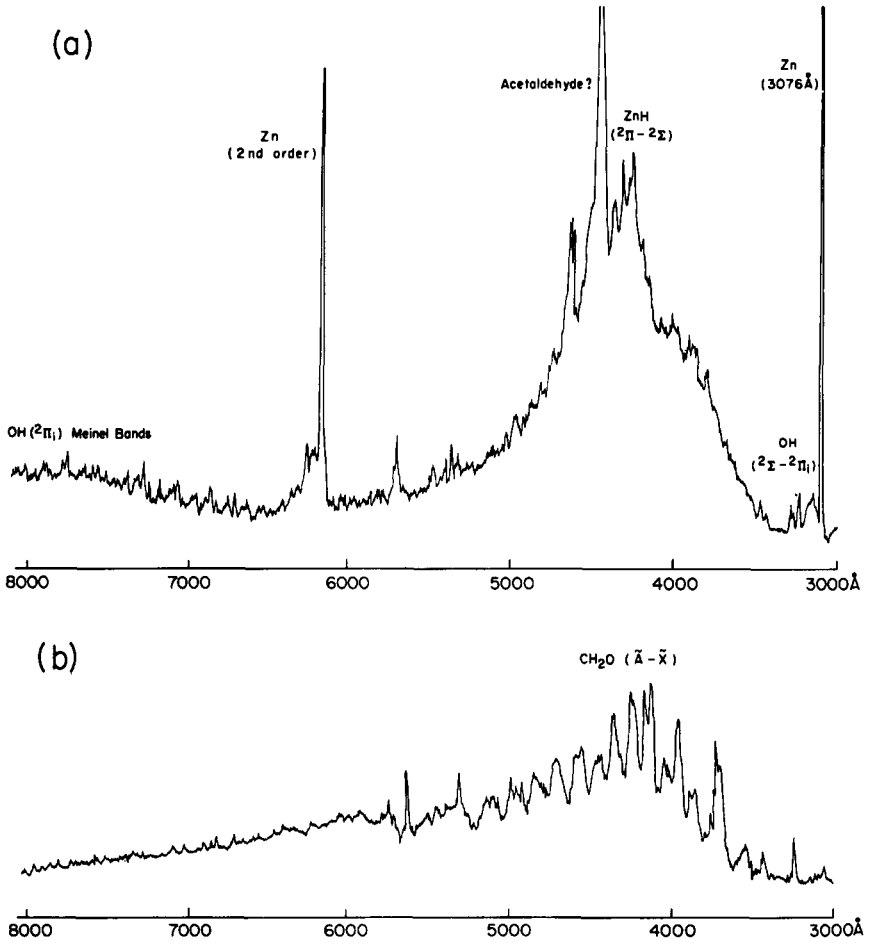

Fig. 2. Chemiluminescent spectra from the reactions of ozone with (a) Zn $(C_2H_5)_2$ and (b) Zn $(CH_3)_2$ at a total pressure ca. 1 torr. Spectrometer band width is ≈10 Å for (a), and ≈15 Å for (b). The detector response is not corrected for wavelength.

known that flames with F_2 as the oxidizer tend to yield higher rotational temperatures [14].

The very intense Zn intercombination line $(^3P_1 - {}^1S_0)$ at 3076 Å may arise from several mechanisms:

$$H + H + Zn \rightarrow Zn\,(^3P_1) + H_2, \quad (4)$$

$$H + OH + Zn \rightarrow Zn\,(^3P_1) + H_2O, \quad (5)$$

$$OH\,(^2\Sigma^+) + Zn\,(^1S_0) \rightarrow OH\,(^2\Pi_i) + Zn\,(^3P_1). \quad (6)$$

The three-body recombinations given in (4) and (5) have been shown by Padley and Sugden [15] to account for the nonthermal excitation of a great number of metal atoms in their flame studies. However, we speculate that (6) may be an important mechanism here because of the close coincidence between the energy levels of the species involved.

The emission of OH in the ultraviolet region has been observed in almost all types of hydrocarbon combustion. Gaydon [16] has suggested the following reaction to account for these observations:

$$CH + O_2 \rightarrow CO + OH^*\,(^2\Sigma^+); \Delta H = -160\ \text{kcal/mole}. \quad (7)$$

Under our operating conditions it is very unlikely that CH could be formed abundantly from the

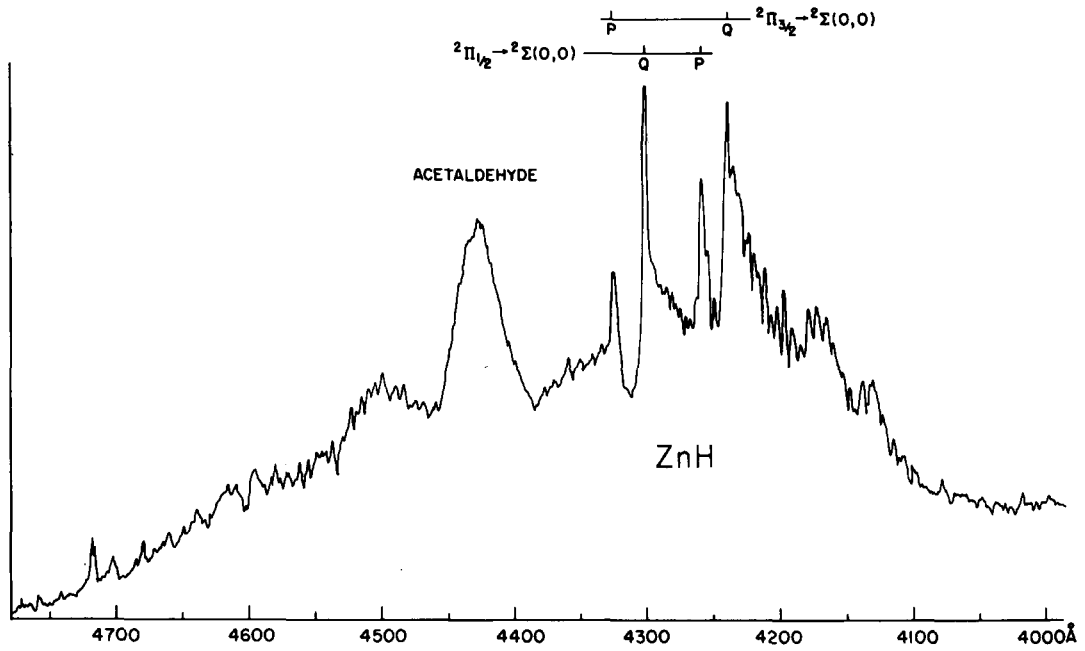

Fig. 3. Chemiluminescent spectrum from the reaction of ozone with $Zn(C_2H_5)_2$ taken with ≈2.5 Å resolution (uncorrected for spectral response). The band heads of ZnH are marked.

decomposition of C_2H_5 · or from subsequent reactions. Therefore, an alternative mechanism must be sought. The observation of $OH(^2\Sigma^+)$ emission in the reaction of H with O_3 has been reported [17, 18]. In his flame study of this reaction at 0.5 to 4.5 torr pressures, Broida [17] finds that the intensity of the ultraviolet radiation ($A^2\Sigma^+ - X^2\Pi_i$) depends upon the square of the intensity of the visible $OH^\dagger$ ($^2\Pi_i$) radiation. Following his procedure, we have plotted the intensity of the (0, 0) Q_2 head of $OH(^2\Sigma^+)$ at 3089 Å as a function of the intensity of the $OH^\dagger$ ($^2\Pi_i$) (9–4) head at 7756 Å. The brightness of the flame is varied by changing the $Zn(C_2H_5)_2$ flow slightly at a total reaction chamber pressure of about 1 torr, while maintaining the O_3 flow constant. We choose the Q_2 head at 3089 Å rather than the R_1 head at 3064 Å because the latter peak is completely obscured by the intense Zn line. The result shown in Fig. 7 reveals qualitatively a square dependence of $OH(^2\Sigma^+)$ on $OH(^2\Pi_i)$. A similar relationship is obtained when the O_3 flow is varied while the $Zn(C_2H_5)_2$ flow is maintained constant.

4. $ZnH(^2\Pi)$

The spontaneous production of $ZnH(^2\Pi)$ in the reaction of O_3 with $Zn(C_2H_5)_2$ was a great surprise to us. Although ZnH emission has been observed by Egerton and Rudrakanchana [4] in a diffusion flame of $O_2 + Zn(CH_3)_2$ at several torr pressures, the emission of metal hydrides from diffusion flames is still considered rare.

An analogous process involving HgH has been documented by Gaviola and Wood [19] and by Beutler and Rabinowitsch [20]. By exciting the Hg atoms in a mixture of Hg vapor and H_2, these workers found the initial reactions to be

$$Hg^* + H_2 \rightarrow Hg + H + H + K.E. \quad (8)$$

$$Hg^* + H_2 \rightarrow HgH + H + K.E. \quad (9)$$

Reaction (9) was deduced from the observation of HgH emission via sensitized fluorescence:

$$Hg^* + HgH \rightarrow HgH^* + Hg \quad (10)$$

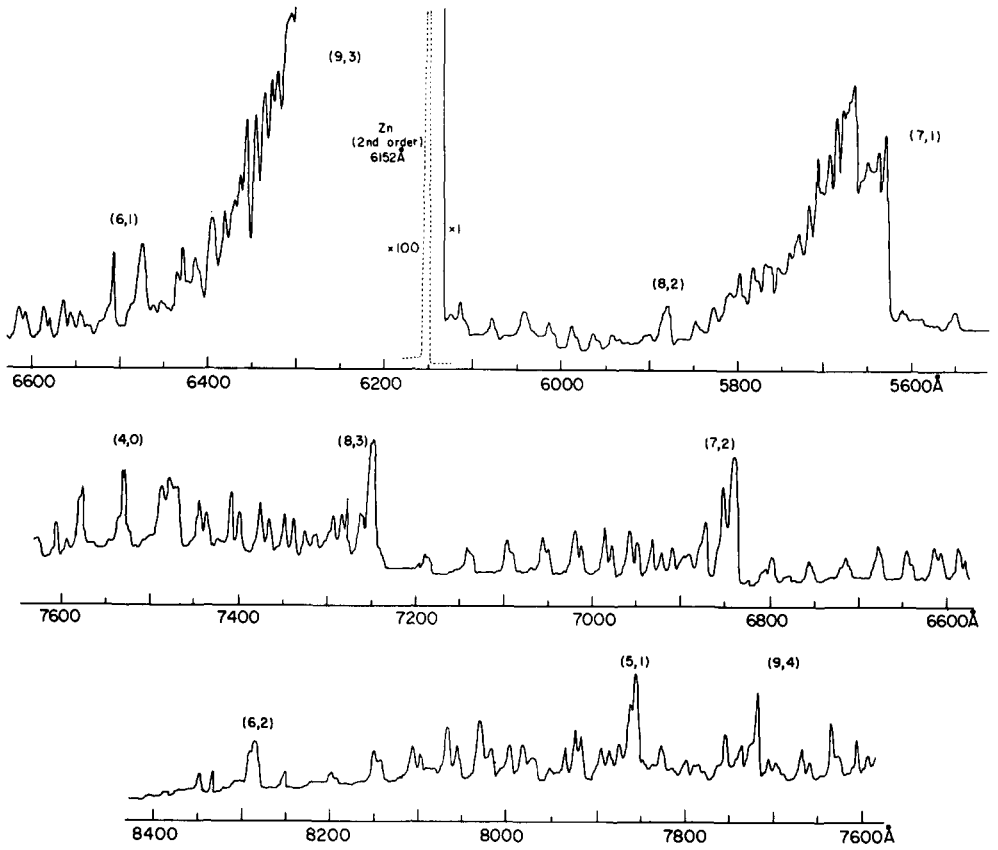

Fig. 4. The vibration-rotation (Meinel) bands of OH ($^2\Pi_i$) from the chemiluminescent reaction of O_3 + Zn $(C_2H_5)_2$ taken with ≈5 Å resolution (uncorrected for spectral response).

In the reaction of O_3 with Zn $(C_2H_5)_2$ the strong emission from $OH^\dagger$ ($^2\Pi_i$) suggests a fair excess of H atoms [See reaction (3)]. The intense Zn emission implies that there is also a relatively high concentration of Zn* atoms. The following reactions therefore suggest themselves for the formation of ZnH*:

$$Zn^*(^3P_1) + H_2(^1\Sigma) \rightarrow ZnH(^2\Sigma) + H(^2S), \quad (11)$$

$$ZnH(^2\Sigma) + Zn^*(^3P_1) \rightarrow ZnH^*(^2\Pi) + Zn(^1S_0), \quad (12)$$

$$\text{or } Zn^*(^3P_1) + H(^2S) + M \rightleftarrows ZnH^*(^2\Pi) + M. \quad (13)$$

B. O_3 + Zn $(CH_3)_2$

This reaction should parallel that of O_3 + Zn $(C_2H_5)_2$, the initial step probably involving the attack of O_3 on the central Zn atom. Figure 2(b) shows the chemiluminescence observed. The species responsible for the emission in the region 3700–4500 Å is readily identified as formaldehyde (CH_2O). In sharp contrast to the reaction of O_3 with Zn $(C_2H_5)_2$, there is no emission from Zn, ZnH, or OH. We believe this is a consequence of the fact that no significant concentrations of H atoms are produced. We attribute this to the different chemical fates of CH_3 and C_2H_5 radicals in the flame.

The cool flame bands of formaldehyde reflect a low flame temperature and are usually associated with the breakdown of peroxides in flames. The lowest excited state of CH_2O requires about 81 kcal/mole for activation. This energy is amply supplied [11] via a reaction analogous to (2)

$$CH_3O\cdot + CH_3O\cdot \rightarrow CH_2O^* + CH_3OH; \quad \Delta H = -96 \text{ kcal/mole}. \quad (14)$$

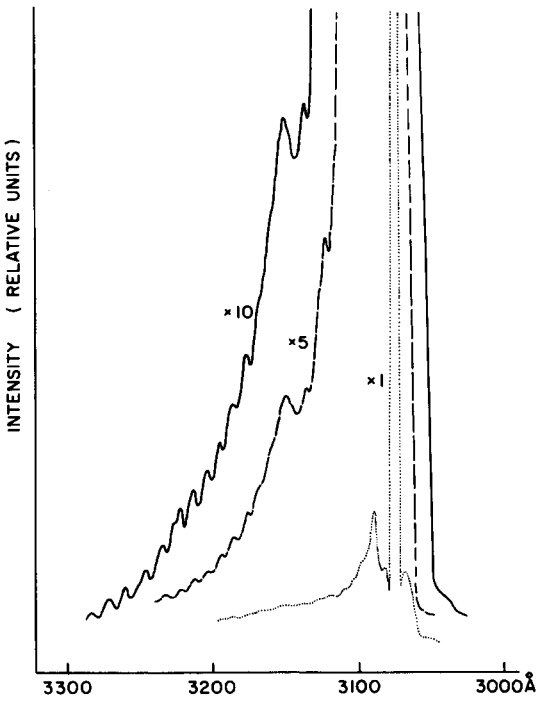

Fig. 5. Some rotational lines of OH, $A\ ^2\Sigma^+ - X\ ^2\Pi_i$, (0, 0) band from the reaction of ozone with $Zn(C_2H_5)_2$. Note how the intense Zn intercombination line (3076 Å) has obscured the R_1 head at 3064 Å.

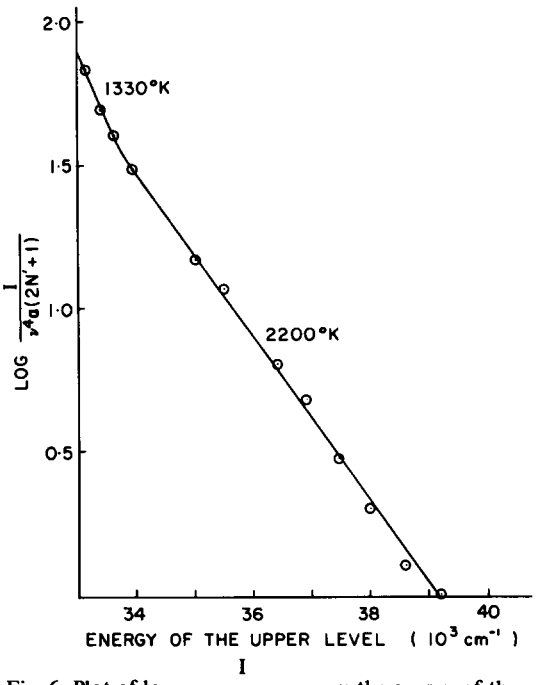

Fig. 6. Plot of log $\frac{I}{\nu^4 a\,(2N'+1)}$ vs the energy of the upper level for the P_2 branch of the OH, $A\ ^2\Sigma^+ - X\ ^2\Pi_i$, (0, 0) band formed in the ozone + $Zn(C_2H_5)_2$ reaction. I is the observed intensity, ν the wavenumber of the observed line, and a $(2N' + 1)$ the transition probability. (Figure 7 follows on p. 34.)

This appears to account for the observed emission.

IV. CONCLUSION

By postulating the initial combustion step of $Zn(CH_3)_2$ and $Zn(C_2H_5)_2$ as the attack of the central Zn atom by O_3, we can see that the resultant flame spectra are markedly different because of the dissimilar chemistry of C_2H_5 and CH_3 radicals in the flame. In the $O_3 + Zn(C_2H_5)_2$ system, there is a significant concentration of H and OH; by contrast, the $O_3 + Zn(CH_3)_2$ system probably yields methoxy radicals as major primary products.

We are extending these investigations to other metal alkyl compounds and we have already observed quite dissimilar behavior for the combustion of metal organics when the organic moiety is methyl or ethyl.

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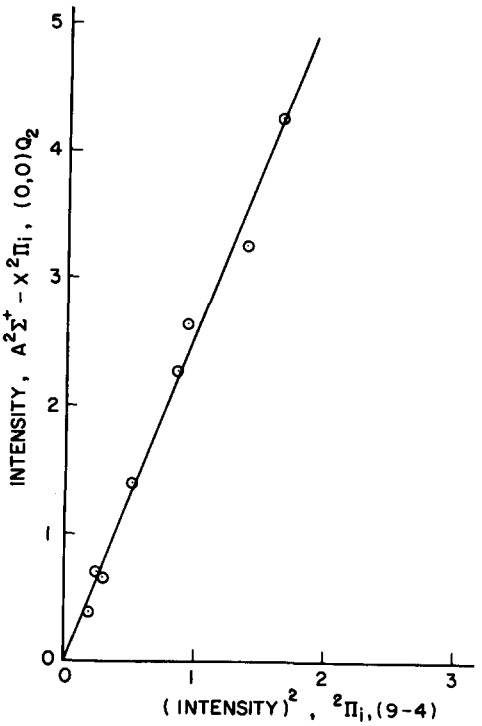

Fig. 7. The intensity of the Q_2 head for the (0, 0), band of the OH $A\ ^2\Sigma^+ - X\ ^2\Pi_i$ system is plotted as a function of the square of the intensity of the OH (9-4) $^2\Pi_i$ transition. The intensities are measured from the $O_3 + Zn(C_2H_5)_2$ flame at a total pressure of one torr.

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